



# The evolution of the dye sensitized solar cells from Grätzel prototype to up-scaled solar applications: A life cycle assessment approach



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## ABSTRACT

Emerging photovoltaics has gathered much attention in the last years. Among the innovative technologies developed in order to decrease the costs and broaden the applicability of photovoltaics, the dye sensitized solar cells have gained a flourishing interest for their potential as an economically and environmentally viable alternative to traditional devices. With the aim to increase the efficiency, stability and lifetime of dye sensitized solar cells, the research and development activity has been very productive in order to find the proper set of materials and the best architectures. This present paper aims to trace the progress of dye sensitized solar cells from a life cycle assessment perspective in order to draw the environmental profile of this technology for assessing its potential for eco-friendly innovation in the energy sector.

The analysis is performed with a cradle-to-gate approach on three different levels: the synthesis of the solar cell main components, the fabrication of modules with different configurations and, finally, the operational phase of a roof-top photovoltaic system. The comprehensive ReCiPe impact assessment method along with the Cumulative Energy Demand, Global Warming Potential and Energy Payback Time indicators were employed to calculate the photovoltaic performances in comparison with other more mature and best-established thin film technologies. Major outcomes, presented along with a statistical analysis, show that dye sensitized solar cells compare similarly and sometimes better than inorganic devices, even for a far-from-optimum industrial fabrication procedure. Such investigation allows pointing out the usefulness of the life cycle assessment methodology to highlight benefits and drawbacks associated with different technical options that have been proposed for the development of the dye sensitized solar cells technology so far.

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## 1. Introduction

During last two decades the development of photovoltaic technologies has lead to the birth of innovative devices defined as “emerging photovoltaic”. These technologies are designed with the aim of decreasing the costs of the module and broadening the applicability of photovoltaic in order to compete with other energy production systems.

Among the new technologies based on alternative materials, those able to mimic photosynthesis by exploiting the capacity of organic dyes to generate electron–hole pairs have gained a flourishing interest for their photovoltaic potential as a viable alternative to traditional inorganic semiconductor-based devices. The leading role in this category is performed by dye sensitized solar cells (DSSCs). The first official reference was reported in a US patent submitted in 1977 [1], but it was the work of Prof. Michael Grätzel on metal oxide sensitization during the 1980s that paved the way for the first efficiently assembled DSSC based on an innovative use of a nanoscopic titanium dioxide ( $\text{TiO}_2$ ) particle layer and a polypyridyl complex of ruthenium as the light absorber in 1991 [2]. In brief, in a DSSC, light is captured by a photosensitizer that is adsorbed on a thin-layer of a nanocrystalline semiconductor (usually  $\text{TiO}_2$ ) placed on the anode. Upon excitation, the photosensitizer transfers an electron to the semiconductor and from there to a back contact; the oxidized dye is subsequently reduced by means of a suitable redox couple, which is in turn reduced at the cathode; finally, a connection between the two electrodes gives rise to an electric current (Fig. 1).

Such solar cells immediately raised a great deal of attention for their versatility and potentially low cost of fabrication: employment of small quantities of inexpensive and readily-available materials produced by well-established processes, possibility of deposition on various substrates, compatibility with printing techniques and integration with a wide range of surfaces are some of the key points in favor of DSSCs.

Moreover, from an operational point of view, DSSCs produce more power when the temperature increases and can harvest light

beams coming from all angles, which allows them to work even in the presence of diffuse light. Finally, DSSCs are characterized by a different mechanistic approach compared with conventional photovoltaics. In the latter a single material is responsible for all the processes taking place in the cell (light absorption, charge generation and transport), in DSSCs such functions are separated and carried out by different components. Consequently, it becomes possible to work on the single components with a large number of technical options to optimize and improve the performances of the whole device.

Based on the Shockley–Queisser limit theory [3], estimations of the maximum power conversion efficiency envisage a  $\approx 20\%$  target feasibility for a single junction DSSC [4].

Twenty three years have passed since the first 7% record with the power-conversion efficiency of small area cells rapidly climbing to 10% in the late 1990s and then very slowly increasing up to 11.9% in 2012 [5], while photovoltaic performances for prototypal larger scale devices were barely approaching 5%. Thus, photovoltaic cells based on organic sensitizers are not yet a mature technology, and their large scale utilization is essentially hampered by their stability. Factors limiting the efficiency of the cells are mostly related to the materials employed but also to the way in which these materials interact within the cell structure or, in other words, to its architecture.

In recent years research activity to find the optimum set of components to increase efficiency, stability and lifetime has experienced much growth but the slow progress obtained and the difficulty relating to the up-scale processes have fostered the idea that DSSCs would have not fulfilled their promise [6]. A new incentive for multidisciplinary work focused on DSSC development has been boosted by the recent efficiency records that finally allow DSSCs to compete with amorphous silicon solar cells at the lab scale [7]. Moreover, from the industrial point of view, in the last five-year period major efforts have been devoted to the manufacturing and engineering of commercial devices that could meet the standards of the PV market for various applications. Several companies have announced the achievement of good

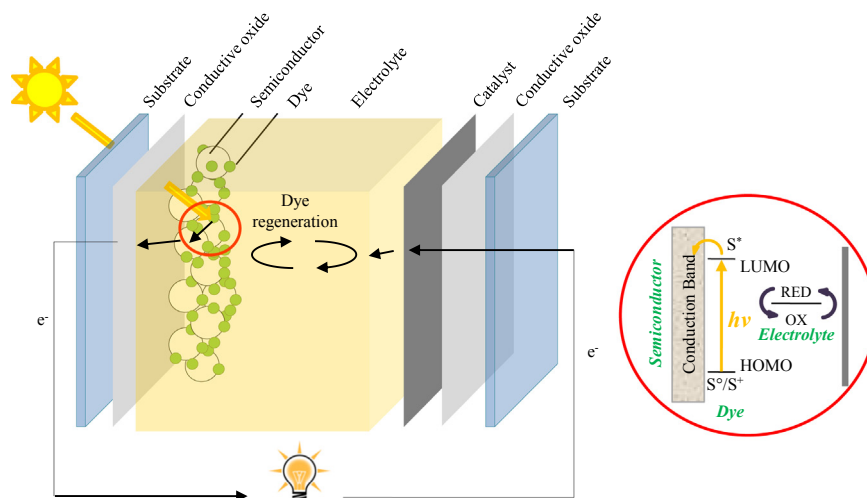


Fig. 1. A sketch of the DSSC structure and operational mechanism.

performing prototypes ready to be launched on the market and investments in MW capacity production plants have been made in several countries.

Many research papers and reviews have been published on DSSCs to date, showing the immense work carried out on this technology. This present paper aims to trace the progress of DSSCs from a life cycle assessment (LCA) perspective with the aim of drawing the environmental profile of this technology for assessing its potential for eco-friendly innovation in the energy sector.

## 2. Development and establishment of DSSC technology in PV market

The highly interdisciplinary research field opened up by the pioneering publication of O'Regan and Grätzel has developed and combined a multitude of materials suitable for DSSCs, as described in several reviews published in the last years [8–13]. In addition to the development of innovative material components, several module configurations and technologies, manufacturing processes and DSSC-specific characterization methods have been introduced. Indeed the very dynamic work in the wide area of DSSC technology is proven by the constantly expanding number of patent applications [14]. To date, several companies have focused their activity on glass-based and flexible DSSC prototype development, production line setting-up, and marketing of specific materials and production equipment [15–27]. Moreover, as DSSC technology is so different from other photovoltaic technologies, it has become possible for industries with little photovoltaic history and large and mid-sized specialty chemical companies (the German BASF and Merck, the Japanese Showa Denko and Fujikura or the Chinese Everlight) to enter a new market segment. This contributes to the huge ongoing work for the optimization of components, device fabrication techniques, module development and various integration and connection solutions.

Among the potential target market areas, the first commercial DSSC applications have been established in the small electronic and mobile device sectors (decorative solar lamps and chargers, flexible mobile phone chargers, solar bags, etc.).

In the past two years, some companies active in the DSSC field have launched some outdoor devices that basically remain niche products that do not yet match the performances guaranteed by other solar cells.

Nevertheless DSSCs have moved out the R&D stage (where, for example, quantum dot and pure organic solar cells remain) and, with the very recent efficiency records reached on the lab scale and the impressive progresses reported for module tests [28–30], this technology is on the verge of approaching the thin film PV market [31].

In a context that has been dominated by traditional silicon-based and, to a minor extent, by inorganic thin film technologies, DSSCs can compete in terms of stable performances in non-standard conditions of temperature, irradiation, and solar incident angle, in economical terms for low-cost manufacturing processes, in terms of quantity and availability of raw materials and, very importantly, in terms of esthetic possibilities for architectural elements and building integration. This latter aspect, coupled with the feasible use of flexible and lightweight substrates, represents an essential advantage of DSSCs with respect to other technologies. The chance to manufacture opaque or semi-transparent multi-colored cells by tuning the sensitizer adsorbed on the photoelectrode opens up the path for many different solutions according to the end use. Energy-producing windows, shingles and panels, building facades and solar roofs based on DSSC could represent solutions for the integration of photovoltaics in places where landscape restrictions have so far limited their application

or, simpler, for fashion reasons. The manageability of these cells could fit the standards for integration in the automobile and nautical sectors and additionally give major input to the intelligent sensors industry.

This kind of applications would clearly address a high-value market segment in the immediate future but, in a realistic perspective of different PV technologies coexistence, these facts corroborate the thesis that DSSCs represent the most promising option for a new paradigm of energy generation systems. Research reports, in fact, forecast a remarkable growth for DSSC technology in next several years [32,33].

The usefulness of such devices is certainly made more evident if rural electrification and developing countries issues are taken into account. Low cost off-grid photovoltaic electricity supplies are suited to greatly improve the situation in those countries with abundant availability of sunshine but poor resources to provide for peoples' basic needs [34,35].

If the stability and efficiency barriers for commercial products can be overtaken ( $> 10\%$ ), DSSCs could compete favorably with other thin film technologies for grid-connected solutions, contending with the already mature amorphous silicon technology. Moreover, in an increasing economy of scale projection, their low cost and ease of production that avoids expensive high vacuum steps should benefit large-scale applications.

Obviously market factors such as the overall demand, scarcity of rare elements and availability of highly purified components will play a key role in the evolution of the photovoltaics future and, in this framework, there are increasing expectations for products that integrate low cost materials to good efficiency and durability. This is one of the reasons why generous governmental funding for the development of innovative technologies has been given in recent years in many countries.

From an economy point of view, there is a general consensus that a \$0.6 per peak Watt reference price for a module must be reached for DSSCs to be competitive with other energy generating systems [10,11]. These considerations are based on the fact that the less efficient solar module would need a larger balance of system (BOS, i.e. all the components necessary for the proper functioning of a photovoltaic system, such as support materials, frame, cables, inverter, batteries, etc.) that clearly increase the costs for installation. Even if DSSCs will not reach the efficiency values typical of other inorganic thin film technologies at module scale in the very near future, thus not being the best competitor in terms of price/Watt, they would certainly represent the most advantageous solution for large surface covering or building integrated applications in terms of price/area. In any case, in order to compete for small-to-large scale power generation, DSSC systems must reach a level of reliability that would make them affordable, compared to other traditional solutions. Indeed, beside the huge effort to minimize system losses, intensive research has been focused on the development of suitable architectures that reduce inherent costs by changing substrates, of simple synthesis routes to manufacture the solar cell components and, ultimately, in searching for alternative cheap materials allowing for good efficiencies.

From a general point of view, any prospect for solar technologies must be considered within the context of the overall PV market that very recently has experienced a slowdown period. Different from what happened in the 2009–2011 period which saw an exploding growth of the market in spite of the worldwide recession, nowadays photovoltaics has begun to suffer from governments reviews and reductions of all those economic measures (subsidies, feed-in-tariffs, tax incentives) that have supported the PV market over the last several years. Practical consequences for future PV market are hardly predictable, but it can be assessed that off-grid applications and the BIPV sector,

where the DSSCs already represent a viable solution [36], are somewhat less economically dependent on subsidies and this could be the opportunity for DSSCs to enter the PV market firmly.

### 2.1. The context of the research

Light harvesting is the first step in the sequence of processes that lead to power generation in DSSCs. The wide band gap semiconductor  $\text{TiO}_2$  is photochemically stable and thus suitable for cathode fabrication, but its spectral sensitivity is limited to the UV. For this reason a light-absorbing sensitizer has to be adsorbed onto the semiconductor surface [37]. Chromophoric compounds suitable to this target must fulfill several requirements for DSSC optimal functioning. These include a broad absorption spectrum, good extinction coefficient, adequate ground and excited energy states, good anchoring to the semiconductor surface, long stability (about  $10^8$  redox turnovers corresponding to about 20 years operational lifetime) and, preferably, no toxicity and low cost of manufacturing.

The synthesis and characterization of new sensitizers with increased efficiency and stability has been furthered and extremely productive in the last years [9,38,39]. Several dye categories have been investigated and tested for DSSC application, including metal complexes, porphyrins and phthalocyanines, and organic dyes. Prior to the very recent record achieved with high-performances perovskite-sensitized solar cells [40], metal complex-based dye molecules, especially ruthenium based complexes, have performed the best for DSSC devices. Such sensitizers have been employed for the pilot scale products commercialized so far because of their relative stability and good efficiency under standard conditions [41]. On the other hand the inherent weakness of these metal complexes is represented by difficult purification procedures, high cost of the metal precursors, scarcity (and consequently, extra cost for potential recycling) and relatively low extinction coefficients. This latter factor requires more sensitizer to be adsorbed onto the nanoporous semiconductor thus leading to a thicker photoelectrode. In these conditions electron injection efficiency, dye regeneration rate and electron transfer to the redox system are strongly affected. The fine-tuning of the sensitizer can address these issues by increasing the molar absorption coefficient and modeling their structure in order to prevent redox species getting too close to the semiconductor surface.

In order to find a trade-off among all this parameters and obtain a broader absorption spectrum, natural or synthetic organic dyes have been proposed as valid alternatives. Compounds characterized by a D- $\pi$ -A architecture, in which a donor group (D) is connected to an acceptor/anchoring group (A) through a conjugated bridge ( $\pi$ ) have gained a particular interest in this area. Upon irradiation, the D- $\pi$ -A arrangement facilitates the generation of photoinduced intramolecular charge-transfer states, thus promoting electron injection into the nanocrystalline semiconductor. So far, a general design rule for optimum organic dyes has not been defined but it's clear that any study on the sensitizer needs to be performed in conjunction with electrolyte and semiconductor film studies to match their electrochemical properties and maximize the energy conversion efficiency of DSSC.

The study presented in this work originates from the results of the FOTOSENSORG Project (POR FSE 2007–2013) that have integrated the experiences of the Department of Chemistry and the Department of Pharmaceutical and Applied Chemistry of the University of Siena, the Laboratories of ICCOM-CNR of Firenze and EXERGY s.r.l. of Arezzo. The multidisciplinary activity has focused on the production of new organic sensitizers for DSSC through the synergy of a computational approach for molecular design and eco-compatible lab strategies for dye synthesis [42–44]. Data and information gained throughout the project were pivotal to plan

and perform an extensive LCA, starting with the manufacturing of key components of a single cell up to the use phase of a virtual domestic photovoltaic installation made of DSSC modules.

The analysis of the environmental performances of DSSC allowed an update of results obtained by previous studies and a comparison with other photovoltaic thin film technologies that have already undergone environmental profile evaluations [45–58]. The aim of the study is the assessment of the sustainability of new solar technologies and the potential for eco-friendly innovation in the energy sector.

## 3. LCA methodology

Life Cycle Analysis (LCA) is a methodology that allows an outlining of the environmental profile of a product, process or service during its whole life cycle, from raw materials extraction to end-of-life and disposal phase. This representation, usually defined as the “cradle-to-grave” approach, is the more extended and beneficial description of a complete LCA; other options are the “cradle-to-gate” or “gate-to-gate” approaches that can be applied depending on the focus of the study or on the availability/scarcity of representative data for a specific phase of the life cycle. LCA is a mathematical approach that accounts for all the material and energy flows characterizing the system under study and calculates the potential environmental impacts associated with the different steps. The methodology is defined and regulated by the International Organization of Standardization with the ISO 14040 and 14044 standards [59,60]. The analysis is divided in four phases: goal and scope definition, inventory analysis (also called Life Cycle Inventory, LCI), impact assessment (also called Life Cycle Impact Assessment, LCIA) and interpretation of results. In the first phase the study model is defined, specifying the methodological framework and cut-off criteria with which all other LCA phases must comply. The second step lists and quantifies the inputs and outputs of the processes at each stage in the life cycle. The impact assessment phase provides an analysis of the system from an environmental point of view. It consists of two mandatory elements (classification, i.e. grouping the material, energy and emissions data collected in the LCI into the selected impact categories, and characterization, i.e. assignment of magnitude to the contribution on each impact category through characterization factors) and a set of optional elements (such as normalization and weighting) that may be used in order to calculate a final single score describing the overall impact of the system. Finally in the interpretation phase, recommendations and conclusion are outlined on the basis of the technical findings and critical points identified through the analysis for the overall improvement of the system.

In this study all calculations were performed with the SimaPro software version 7.3.3, developed by PRè Consultants [61]. When primary data were not available, the main database used for the analysis was the Ecoinvent version 2.2 [62].

### 3.1. Impact indicators assessment

In the LCIA phase, the environmental loads connected with all the LCI data are identified and evaluated. The purpose is to translate the input and output flow data collected in the inventory into an assessment of the critical effects on impact categories by summing up the whole environmental burden in a few clear indicators. The LCA methodology allows for the use of many different LCIA indicators and each of them is focused on a different environmental issue.

First of all, for the characterization of the several case study phase impacts, we employed the ReCiPe method that allows

performing the study at an impact (mid-point) or damage (end-point) category level [63]. The environmental analysis reported in this work is performed with the ReCiPe 2008 endpoint level approach associated with a hierarchist perspective. The 17 category indicators of ReCiPe endpoint level approach are Fossil Depletion, Metal Depletion, Natural Land Transformation, Urban Land Occupation, Agricultural Land Occupation, Marine Ecotoxicity, Freshwater Ecotoxicity, Terrestrial Ecotoxicity, Freshwater Eutrophication, Terrestrial Acidification, Climate Change Ecosystems, Ionizing Radiation, Particulate Matter Formation, Photochemical Oxidant Formation, Human Toxicity, Ozone Depletion, Climate Change Human Health.

Secondly, to have a more detailed comparison of the environmental performances of each technology analyzed, we employed three additional indicators, typical for photovoltaic energy systems analysis.

#### 3.1.1. Cumulative Energy Demand

The Cumulative Energy Demand (CED) is an energetic indicator that quantifies the whole energy requirement during the life cycle of a product. It is expressed in equivalent of MJ of primary energy and it sums up both direct energy (like electricity, thermal energy, etc.) and indirect energy contributions (embodied energy of materials) [64].

#### 3.1.2. Global Warming Potential

The Global Warming Potential (GWP) method, developed by the International Panel of Climate Change (IPCC), assesses the impact of the whole life cycle on global warming in terms of equivalent of carbon dioxide (CO<sub>2</sub>). In this work the GWP method on a time horizon of 100 years is used [65].

#### 3.1.3. Energy Payback Time

The EPBT is an energetic indicator widely used to compare different types of energy production technologies, like photovoltaics [47,48,53,55–57,66–70]. It is expressed in years and represents the time required for the system to generate the same amount of energy consumed in all production processes. The calculation process is reported below.

$$\text{EPBT} = \text{CED} / \text{YEO} \cdot C \quad [\text{year}]$$

With CED is the Cumulative Energy Demand [MJ<sub>prim</sub>], YEO is the Yearly Energy Output [MJ<sub>prim</sub>/year] and C is the electrical conversion factor [MJ<sub>el</sub>/MJ<sub>prim</sub>].

The calculated YEO for the case study is shown in Section 4.3. The conversion coefficient has been set to 0.31, a value typical for Western Europe [49].

Monte Carlo analysis has been performed in order to define the uncertainty range in the LCA analysis calculations for the organic synthesis, cell and module assembling steps for DSSC technology. A 10,000 runs criterion and a 95% confidence interval have been selected in order to evaluate the accuracy of the indicator values. The statistical data regarding each single impact indicator (uncertainty range, mean, standard deviation and coefficient of variation) are reported in following separated tables.

## 4. LCA case study and assumptions

The main goal of this work is the environmental assessment of various DSSC configurations that can be employed for module fabrication and the comparison of their environmental performances with other thin film technologies. The study consists of a cradle-to-gate analysis that starts with the production of raw materials for the fabrication of a single cell and ends up with the use phase of a DSSC domestic photovoltaic installation. At this level the end-of-life phase has not been included in the analysis for lack of data; considerations on the possible pathways for convenient options for dismantling, disposal and recycling are discussed in Section 6 of this manuscript and will be taken into account in a following work. System boundaries for the case study are shown in Fig. 2.

### 4.1. Sensitizer production

The starting point of the analysis is the laboratory organic synthesis of three different dyes chosen as representatives of the many sensitizers that have been employed for DSSCs: the ruthenium based dye N719 [71–74], the organic metal-free dye D5 [75,76] and the Zn-porphyrin dye YD2-o-C8 [77]. These molecules are characterized by high photoelectric conversion efficiency and have been taken as a reference because of the good photovoltaic performances achieved by modules sensitized with these compounds. The main goal of this investigation is the comparison of the environmental profiles of the three sensitizers to identify the benefits and drawbacks related with the use of metal and metal-free compounds. The chosen functional unit is 1 g of dye produced on the laboratory scale. The synthetic strategy has been modeled on

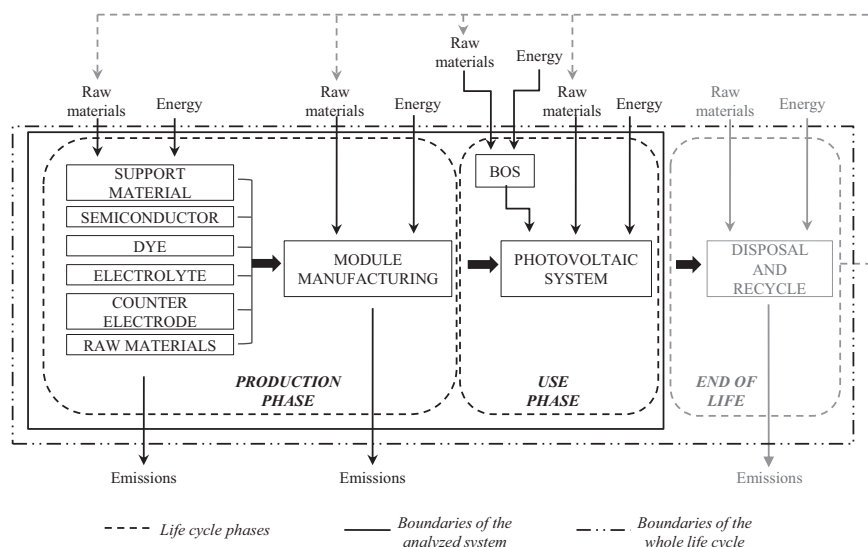


Fig. 2. Flow-chart scheme and boundaries of case study life cycle phases.

the basis of data published in the literature. As no specific pre-industrial process data information are publicly available, in order to perform a correct evaluation of the contribution on the overall impact of module fabrication we attempted to reproduce a *kilo-lab* scale process for the analysis. Thus the yield of the organic dye syntheses was set to 89%. The scale-up of the input flows was computed to obtain 100 g of dye. To this aim, we performed an analysis based on scaling relationships in order to assess the contribution of material and energy inputs to the overall impacts [78,79]. For such laboratory syntheses, energy consumptions do not scale isometrically with the final product mass, so we used weighted energy inputs depending on the particular instruments or machinery employed for the production. On the other hand, material inputs were scaled linearly with the final product mass and yield of reaction. We observed that the threshold for the dependency of calculated impacts on synthesized quantity was 100 g, thus we chose this mass scale production as the reference to model the life cycle inventory of this analysis phase. No allocation rules were defined for direct energy inputs. It must be underlined that laboratory machinery and instruments are not completely dedicated to the synthesis of a single product during their own life cycles. In general the risk of such assumptions is an overestimation of the energy effectively consumed for the processes analyzed in the study. At this level of the analysis, however, this choice did not considerably affect the final results, as will be showed in Section 5.1. Primary data for the synthesis of metal free organic dye (D5) such as information concerning reaction times, power of lab machinery, solvents and eluents quantities were set on the basis of the procedures developed by the laboratories involved in the Fotosensorg project. Data for the synthesis of N719 and Zn-porphyrin were taken from scientific literature and patents. Processes for reactants not present in the Ecoinvent 2.2 database were built on the basis of the stoichiometry of reactions described in the scientific literature. For all synthetic strategies, secondary data were taken from the Ecoinvent 2.2 database. Waste flows were considered to be collected for disposal by incineration. The electricity mix employed for the synthetic process is the European Energy mix (UCTE), in order to obtain an analysis independent from the geographical area of production. Transports were not included in the analysis.

#### 4.2. Cell and module

The next step of the study is focused on the industrial production process for the manufacturing of a DSSC module. The goal of this step is the characterization of the hot-spots in the production chain of several types of DSSC modules to highlight the opportunities of implementation for any of the investigated device.

The DSSC industrial production process is very similar to those employed for the production of other thin-film technologies modules and it does not require the assembly of several single cells but it is based on the direct fabrication of a working module. At this level, data available in the literature and in web resources are not precisely referred to the fabrication of a module, thus the LCI has been built taking into account several assumptions. Material inputs were linearly scaled starting from quantities required for the single cell assembling. Energy inputs were weighted on the basis of publicly available information about instrumentation and machineries for pilot scale production. This approach was chosen in order to avoid an overestimation of input flow contributions to the reference unit process in the absence of an optimized industrial production for these devices [28,46,80–90].

The production processes of all the inputs necessary for the fabrication of the module have been built referring to the functional unit of a  $60 \times 100 \text{ cm}^2$  frameless panel. LCI compiling and LCA analysis of the production phase have been performed for each component of the cell/panel similarly to the sensitizer.

It must be underlined that, very often, for a single configuration several fabrication strategies have been proposed by many research institutes and companies. Moreover, depending on the particular configuration to be manufactured, the technical options for a manufacturing strategy are various. In this analysis the steps of module production were modified appropriately depending on the chosen DSSC configuration.

The main steps characterizing the production process of a DSSC module in the Grätzel prototype standard configuration can be summarized as follows: glass substrates coating; laser etching; deposition of active layers; sintering; staining; substrates matching; electrolyte filling.

The manufacturing scheme of the DSSC module selected as a reference to build the LCI starts with the preparation of the two glass substrates coated with a low resistance and high optical transmission fluorine-doped tin oxide (FTO). Hole drilling is required to obtain holes for electrolyte filling and subsequently the two glass plates are washed using appropriate detergents (i.e. isopropanol). The following step is the laser-scribing of the substrates to remove the conductive oxide layer so that *in-series* or *parallel* connected tile can be produced. A colloidal  $\text{TiO}_2$  solution containing particles of desired size is screen-printed on the photoelectrode, whereas platinum solution is printed on the counter electrode and a silver grid is screen-printed on both the photo and counter electrode. After deposition, the substrates are dried and the  $\text{TiO}_2$  coated photoelectrode is fired in a furnace in order to sinter the semiconductor. The next step consists of coloration of the photoelectrode by staining it in a dye solution so that photosensitizer molecules can absorb onto the  $\text{TiO}_2$ . After washing, the two substrates are adequately positioned and fused in an oven and, in the final step, an electrolyte solution is purged through the filling holes which are sealed afterwards.

In Table 1 raw materials selected for the LCI of the DSSC module are reported. Specific quantities have been computed through the up-scale procedure defined on the basis of lab data and information available in the literature [80].

The industrial steps required for module production process are similar for all the configurations and this is basically valid also for material inputs. Substantial differences are related to the use of different sensitizers and, consequently, the electrolyte employed, as in the case of the porphyrin dye and the cobalt-based redox couple [77].

The assessment of the environmental performances for different module configuration has been performed fixing the sensitizer (ruthenium-based dye), the semiconductor (nanocrystalline  $\text{TiO}_2$ ) and contacts material (silver paste), and varying other material components. This approach was chosen to compare those configurations with the best photovoltaic performance records reported in the literature.

Energy inputs have been calculated on the basis of machineries and instruments data published by industries and technical information given by research institutes involved in DSSC field.

Many innovative materials proposed as alternatives to those listed in Table 1 have been evaluated in this work. A great deal of

**Table 1**  
LCI for frameless dye sensitized solar module ( $60 \times 100 \text{ cm}^2$ ).

Materials	g/m <sup>2</sup>	Reference
FTO glass substrate (× 2)	10,000 (× 2)	[46,91,92]
Isopropanol	1315	Study assumption
Semiconductor $\text{TiO}_2$	15	[74,80,93,94]
Glass fiber	7.2	Study assumption
Platinum counter-electrode	15.8	[74], Lab data
Silver paste	7.2	[46]
Dye	0.1	[46], Lab data
Electrolyte	24	[46,74,77,80,95–98]

research on the design of photosensitizers has contributed to the development of an enormous number of dyes with different chemical structures [9,38,115,116]. Regarding semiconductors, several further options instead of  $\text{TiO}_2$  have been proposed such as zinc [9,115,117–119], tin, magnesium and aluminum oxides [9]. Semiconductor mixtures and doped semiconductors have also been tested [9,115]. Good results for efficiency increase have been recently achieved with niobium oxide [120]. Concerning the physical structure of the semiconductor, the use of  $\text{TiO}_2$  nanotubes and nanorods have proved to be effective for increase of electron transport [9,115,121].

Another component allowing for a wide range of different choices is the electrolyte. This can be varied both for the redox couple used ( $\text{I}^-/\text{I}_3^-$ ,  $\text{Co}^{2+}/\text{Co}^{3+}$ ,  $\text{Br}^-/\text{Br}_3^-$ , SCN group) and for the nature of the solution [74,77,95–100]. In this respect, there is much research focused on the development of ionic liquids, quasi solid and solid electrolyte, in attempts to overcome issues such as corrosion of the semiconductor/dye system, volatility and stability of the redox couple system, sealing degradation and so on [36,122–128].

For the production processes, secondary data were taken from the Ecoinvent 2.2 database. No waste flows were considered for this step of the analysis. The electricity mix employed for the manufacturing process is the European Energy mix (UCTE), in order to obtain an analysis independent from the geographical area of production. Transports were not included in the analysis considered (Table 2).

**Table 2**  
DSSC configuration representatives considered in this study.

Configuration	References	Abbreviation
Glass–liquid electrolyte–platinum–glass	[74,80]	A
Glass–ionic liquid (type 3)–platinum–glass	[74,80,99,100]	B
Glass–ionic liquid (type 6)–platinum–glass	[74,80,95,100]	C
Glass–ionic liquid (type 7)–platinum–glass	[74,80,95,100,101]	D
Steel–liquid electrolyte–platinum–glass	[74,80,102–105]	E
Steel–liquid electrolyte–platinum–PET	[74,80,102,106–108]	F
PET–liquid electrolyte–platinum–glass	[74,80,106–109]	G
PET–liquid electrolyte–platinum–PET	[74,80,106–108,110]	H
Glass–ionic liquid (type 1)–cobalt sulfide–PET	[74,80,95,100,106–108,111]	I
Glass–liquid electrolyte–carbon	[74,80,112–114]	L

**Table 3**  
PV thin film technologies considered for the LCA analysis.

PV thin film technologies	References
Amorphous silicon (a-Si)	[67,68]
Copper indium diselenide (CIS)	[52,67,68]
Cadmium telluride (CdTe)	[52,67,68]
Micromorph (MCPH)	[51]
Polymeric	[134]

**Table 4**  
PV thin film technologies considered for the LCA analysis.

Type	Lifetime years	Cell efficiency %	Panel efficiency %	Cell area $\text{m}^2$	Cell number Unit/ $\text{m}^2$	Area 3 kWp $\text{m}^2$	Active area $\text{m}^2$
a-Si	20	6.5	6.5	1	1	46.5	46.5
CIS	20	10.7	10.7	1	1	28.1	28.1
CdTe	20	10.9	10.9	1	1	27.5	27.5
MCPH	20	8.74	8.74	1	1	34.32	34.32
Polymeric	20	6	5	1	1	60	60
DSSC glass	20	10.2	8	1	1	51.2	38.4
DSSC PET	20	8.1	8	1	1	51.2	38.4
DSSC steel	20	8.3	8	1	1	51.2	38.4

### 4.3. Photovoltaic installation

In the last step of the analysis, the DSSC devices are compared with other thin film modules in order to assess their environmental sustainability. To perform this comparison, three configurations were selected (A, E, H) as representatives of the DSSC technology on the basis of the prototypes effectively produced and commercialized at pilot scale and the industrialization potential for final application of these modules.

The analysis has been developed taking as reference a virtual 3 kWp roof-top integrated grid-connected system. The chosen functional unit is the kWh of electricity delivered to the grid. For the DSSC installation, the photoconversion efficiency was set to 8% and thus a panel area of  $12.8 \text{ m}^2/\text{kWp}$  was considered. The chosen efficiency value is considered reliable on the basis of recent engineering achievement announced by some manufacturers [80,87,101,129,130] and forecast development for technical architectures [17,131]. As of now, the modules efficiency is quite low due to the high loss of active area when the total area increases. The active area of the DSSC module assessed in this work was set at 75% of the total area (to date the maximum is 48%).

In Table 3, thin film photovoltaic technologies selected for the comparison are reported: amorphous silicon (a-Si), copper-indium-diselenide (CIS), cadmium telluride (CdTe), micromorph (amorphous silicon+crystalline silicon, MCPH) and polymeric. To take into account most of the data published in the literature, several works were referenced with the aim of harmonizing all results and providing a specific reference for each technology.

To compare the environmental profiles on a common operating condition basis, the BOS was included in the analysis [132,133]. LCI of BOS for DSSC, MPCH and POLYMERIC was built with primary data coming from a previous study by these authors [51]. BOS data for a-Si, CdTe and CIS were taken from the Ecoinvent database [68].

A 20 years period was set as the lifetime for all technologies. All parameters employed in the analysis are reported in Table 4 for each technology. The EPBT is strictly correlated with the yearly production of electricity (YEO); this is determined by several factors depending on the technology and the geographical installation:

$$\text{YEO} = I \cdot \text{AA} \cdot \eta \cdot \text{PR} \quad [\text{kWh}/\text{year}]$$

With  $I$  is the average yearly irradiation [ $\text{kWh}/\text{m}^2/\text{year}$ ],  $\text{AA}$  is the active area [ $\text{m}^2$ ],  $\eta$  is the conversion efficiency [%] and  $\text{PR}$  is the performance ratio [%].

The PR represents the thermodynamic energy losses due to the resistance of the BOS. Generally the reported PR value for standard BOS is 80% [135,136] but in this case a conservative value of 75% for all installations was assumed [70]. Apart from the values of active area and conversion efficiency that are specific for each technology, the average yearly irradiation plays a key role for energy production [137]. For a broad and complete evaluation of the photovoltaic performance and in order to restrict the uncertainty due to

**Table 5**

Calculation of YEO for a virtual roof-top DSSC photovoltaic system installed in Central Europe ( $I = 1117 \text{ kWh/m}^2 \text{ year}$ ,  $PR = 75\%$  and  $\text{area} = 12.8 \text{ m}^2$ ).

Years	$\eta$ %	YEO kWh
1	8.000	857.86
2	7.920	849.28
3	7.841	840.78
4	7.762	832.38
5	7.685	824.05
6	7.608	815.81
7	7.532	807.65
8	7.457	799.58
9	7.382	791.58
10	7.308	783.67
11	7.235	775.83
12	7.163	768.07
13	7.091	760.39
14	7.020	752.79
15	6.950	745.26
16	6.880	737.81
17	6.812	730.43
18	6.744	723.12
19	6.676	715.89
20	6.609	708.73

geographic localization of the system, in this study the three average yearly irradiances in Europe were considered:  $1700 \text{ kWh/m}^2 \text{ year}$  for the South Europe,  $1117 \text{ kWh/m}^2 \text{ year}$  for the Central Europe and  $950 \text{ kWh/m}^2 \text{ year}$  for the North Europe [67,68].

In order to make the YEO comparable and reliable among all the technologies, it was assumed photoconversion efficiency losses of 1% per year to simulate the degradation of materials present in the DSSC (Table 5) and MCPH systems. For all other technologies, a decreased yield over lifetime is taken into account with yield data based on production statistics [68]. Transports were not included in the analysis considered.

## 5. Discussion of results

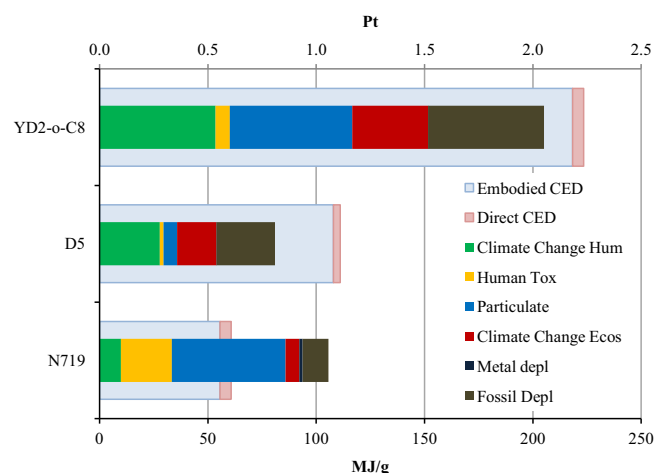
### 5.1. Dyes

In Fig. 3, the environmental profiles of the three dyes synthesis calculated with CED (the histogram in the background) and ReCiPe (in the foreground) are shown. In these diagrams a 1% cut-off has been applied to show only categories with relevant impacts on the synthetic process.

The main reason for environmental impacts calculated with the ReCiPe is the high consumption of solvents and eluents during the synthesis. This applies particularly for the two purely organic compounds (D5 and YD2-o-C8), while the impact of the ruthenium dye synthesis is mainly due to the metal center contained in the molecule.

Regarding the energy consumption assessed with CED, as stated in the assumptions section, it can be seen that the direct energy contributions account minimally in the total CED (2.2% for YD2-o-C8, 2.9% for D5 and 9.2% for N719) even though no allocation rules were taken into account.

The best environmental performance is given by the N719 dye due to the high optimization of the organic synthesis. Furthermore the production process of the ruthenium based dye requires less solvents and eluents and this causes a significant reduction of the embodied energy that is accounted with the CED method. These advantages, coupled with a fair photoconversion efficiency and a quite good resistance to degradation, favored the wide use of N719



**Fig. 3.** Diagrams of CED and ReCiPe for the organic synthesis of the three dyes.

**Table 6**

Uncertainty analysis of CED indicators for the organic synthesis of the three dyes.

	Indicator	Range	Mean	Standard deviation	Coefficient of variation
	MJ	MJ	MJ		%
<b>YD2-o-C8</b>	223.4	202.1–257.7	224.4	16.2	7.2
<b>D5</b>	111.1	103.3–128.2	111.2	7.9	7.1
<b>N719</b>	60.7	46.6–81.7	61.8	9.0	14.6

**Table 7**

Uncertainty analysis of ReCiPe single score indicators for the organic synthesis of the three dyes.

	Indicator	Range	Mean	Standard deviation	Coefficient of variation
	Pt	Pt	Pt		%
<b>YD2-o-C8</b>	2.05	1.88–2.35	2.08	0.13	6.2
<b>D5</b>	0.81	0.75–0.93	0.81	0.05	6.2
<b>N719</b>	1.06	0.81–1.55	1.07	0.23	21.4

which has become one of the most used dyes in prototype and pre-industrial DSSC module production.

Concerning the organic dye syntheses, a further optimization of the synthetic strategies would clearly allow for a global impact reduction and energy saving. Indeed, differently from porphyrins production, there is a wide margin for improving the synthesis of D- $\pi$ -A organic dyes for DSSC through the set-up of flexible chemical procedures requiring less energy intensive steps and eco-compatible raw-materials. The uncertainty analysis results for the organic synthesis of the three dyes are reported in Tables 6 and 7.

The large ranges calculated for the CED and ReCiPe indicators of the N719 dye are due to the presence of ruthenium in the molecular structure; in fact the uncertainty associated to this metal in the Ecoinvent database is high and its contribution gives remarkable effects on the Monte Carlo simulations.

### 5.2. Module

The analysis of the environmental profiles of the module manufacturing process started with the comparison of the production of three modules containing the N719, D5 and YD2-o-C8 dyes respectively. In Figs. 4–6 the environmental impacts

characterization for the three modules production processes using the ReCiPe 2008 method are reported.

In all cases the major impact on all the environmental categories is due to the support material (solar FTO glass in these configurations) which is the preponderant component in terms of mass of a module. Regarding dye contributions to the impact categories characterization, N719 effect is observable in all of the environmental issues analyzed, with the exception of the Ozone Depletion category for which the contribution is negligible. On the contrary, for D5 and YD2-o-C8 the effect on this category is quite relevant due to the massive use of solvents and eluents during

their syntheses. The electrolyte contribution to the same environmental issue almost disappears for the module fabricated with the  $\text{Co}^{2+}/\text{Co}^{3+}$  redox couple because its synthesis requires less organic solvents (mainly trichloromethane) than the  $\text{I}^-/\text{I}_3^-$  redox couple-based electrolyte. For Human Toxicity, D5 gives negligible contribution to the characterization followed by the YD2-o-C8 that gives a restricted effect, while N719 gives a fair contribution due in particular to the presence of ruthenium. The latter is clearly responsible for the remarkable contribution of N719 to the Metal Depletion category.

In the following part of the study, the analysis focused on the assessment of the environmental impacts of different module configurations designed as specified in Section 4.2. In Fig. 7 the results of the life cycle impacts single score analysis for production processes using the ReCiPe 2008 are reported. In the following diagram a 1% cut-off has been applied to show only categories with major impacts on the production process.

The calculated environmental profiles point out a large impact reduction related to the choice of substrate materials. The substitution of glass with PET gives lower impacts for all the categories, while the use of steel for the solar cell back contact produces larger contributions principally to the Fossil Depletion and the Climate Change Human Health categories. The substitution of liquid electrolyte with an ionic one does not generate a large change in the overall impact profiles. However, the transition from liquid to ionic/gel and progressively to solid electrolyte will be pivotal for the increase in stability and the development of DSSC on flexible substrates. In Table 8 the uncertainty analysis for the ReCiPe single score indicators are reported.

In Fig. 8 the GWP100 (red point) and CED (histogram) indicator results for production processes are reported. From the inspection of the graph, a CED ranging between 229 and 1010 MJ for the production of the DSSC module can be outlined. Differences are determined mainly by the embodied energy of raw materials and, to a minor extent, by the direct energy consumed for the manufacturing of modules that is strongly correlated with the support materials used and thus the process temperature and techniques that can be employed.

The main industrial advantage for the manufacturing of DSSC module is the decrease of energy consumptions during the production steps. Different from other thin film technologies that require a high purity level for semiconductors to operate with suitable efficiencies, DSSCs do not need highly energy intensive production processes. Low temperature printing processes, like screen printing or roll-to-roll coating for semiconductor deposition on the substrate are actually employed for the pre-industrial



Fig. 4. Characterization diagram of DSSC module (structure as in Table 1 with N719 dye and  $\text{I}^-/\text{I}_3^-$  redox couple).

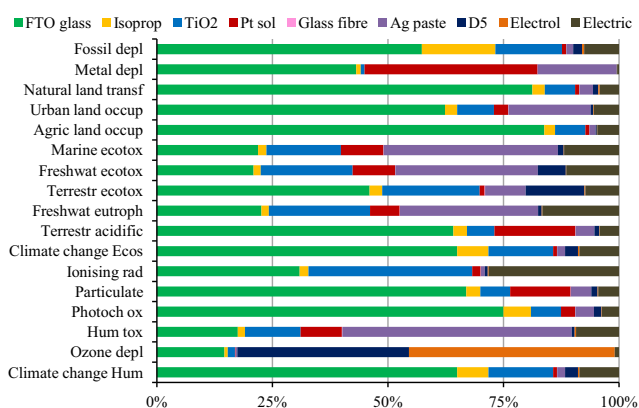


Fig. 5. Characterization diagram of DSSC module (structure as in Table 1 with D5 dye and  $\text{I}^-/\text{I}_3^-$  redox couple).

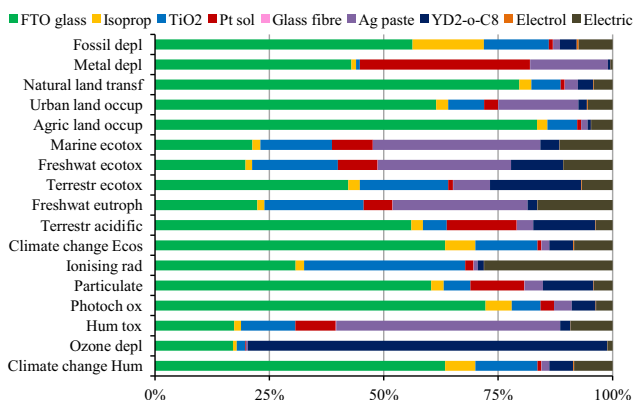


Fig. 6. Characterization diagram of DSSC module (structure as in Table 1 with YD2-o-C8 dye and  $\text{Co}^{2+}/\text{Co}^{3+}$  redox couple).

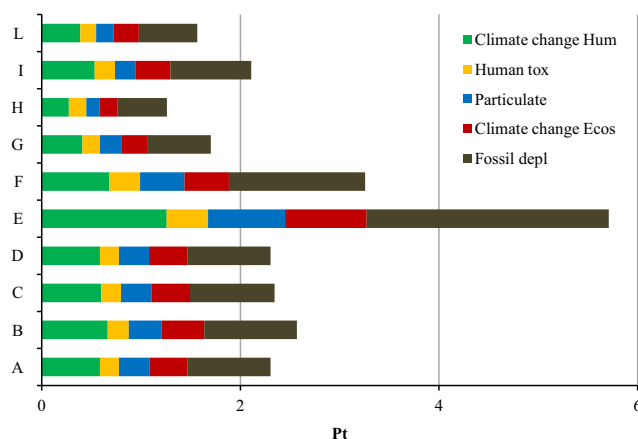


Fig. 7. Diagram of ReCiPe 2008 single score analysis for DSSC modules configurations.

**Table 8**

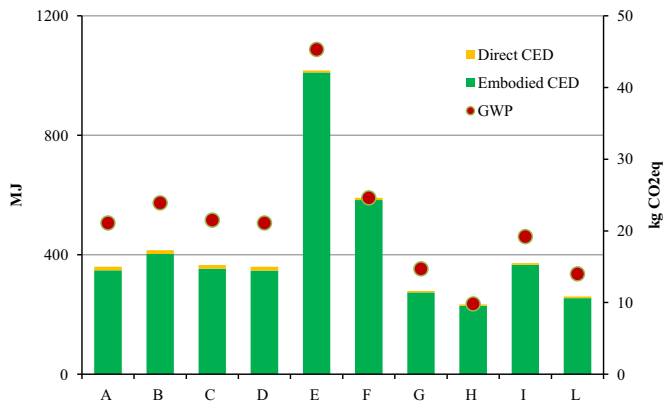
Uncertainty analysis of ReCiPe single score indicators for DSSC modules configurations.

	Indicator	Range	Mean	Standard deviation	Coefficient of variation
	Pt	Pt	Pt		%
A	2.33	1.92–2.87	2.34	0.25	10.9
B	2.60	2.15–3.22	2.62	0.38	14.6
C	2.37	1.96–2.95	2.39	0.27	11.2
D	2.33	1.92–2.88	2.35	0.27	11.4
E	5.74	5.31–6.44	5.81	0.31	5.3
F	3.27	3.02–3.74	3.31	0.21	6.5
G	1.72	1.47–2.09	1.74	0.23	13.1
H	1.27	1.11–1.55	1.28	0.17	13.6
I	2.13	1.82–2.58	2.15	0.21	9.6
L	1.58	1.33–1.96	1.59	0.19	11.7

**Table 9**

Uncertainty analysis of CED indicators for DSSC modules configurations.

	Indicator	Range	Mean	Standard deviation	Coefficient of variation
	MJ	MJ	MJ		%
A	360.1	290.4–444.7	360.1	39.0	10.8
B	415.1	337.4–508.3	415.1	43.8	10.6
C	365.9	296.6–452.6	366.9	40.2	11.0
D	360.0	290.0–445.4	360.0	39.3	11.0
E	1017.1	927.5–1122.2	1020.1	49.9	4.9
F	590.6	539.0–651.8	590.6	28.7	4.9
G	279.0	237.1–330.7	278.0	23.9	8.5
H	233.8	206.3–268.2	234.8	15.8	6.8
I	371.8	332.0–444.8	371.8	33.8	9.1
L	260.5	215.0–316.3	260.5	25.8	9.9



**Fig. 8.** Diagram of CED and GWP100 calculated for DSSC modules configurations. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

production. In Tables 9 and 10 the uncertainty analysis for the CED and GWP100 indicators are reported.

### 5.3. Photovoltaic installation

The final step of the analysis was focused on the comparison of DSSC module performances with other thin film modules. Several LCA study on thin film technologies have been published in the literature. LCA studies on DSSC and organic solar cell technologies have been performed in the past years and they have been taken into account to compare results coming from this study.

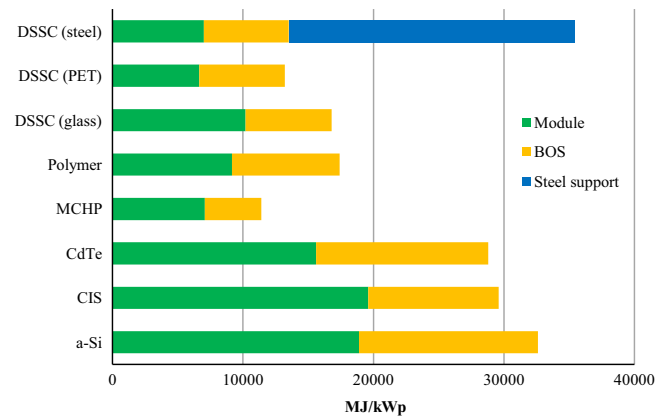
In order to assess the environmental profile of the selected technologies, a virtual 3 kWp roof-top integrated installation connected to the grid was assumed.

In Fig. 9, the CED indicator computed on the basis of the electric productivity (kWp) of the photovoltaic systems is reported. Results are displayed on the basis of the global energy impact shares of module principal components. Clearly there is a sizable contribution given by the BOS for all the installations, but the values are certainly overestimated for DSSC technology. In fact, the LCI for the BOS has been compiled in order to assess the contribution of this component on the global impact as consistently as possible through the analysis. It must be underlined, that potential applications for DSSC technology are quite different compared to other thin film photovoltaics. The opportunities to exploit DSSC for integrated photovoltaic architectural elements and thus even on vertical surfaces not necessarily exposed to the outside, require a new concept of framing, cabling and connection engineering that is still in development [138–140].

**Table 10**

Uncertainty analysis of GWP100 indicators for DSSC modules configurations.

	Indicator	Range	Mean	Standard deviation	Coefficient of variation
	kg CO <sub>2</sub> eq	kg CO <sub>2</sub> eq	kg CO <sub>2</sub> eq		%
A	21.1	17.1–26.3	21.1	2.36	11.2
B	23.9	19.5–29.6	23.9	2.58	10.8
C	21.5	17.5–27.0	21.5	2.43	11.3
D	21.1	17.0–26.6	21.1	2.44	11.6
E	45.3	41.5–49.7	45.3	2.02	4.5
F	24.6	22.6–27.0	24.6	1.11	4.5
G	14.7	12.4–17.7	14.7	1.34	9.1
H	9.8	8.7–11.3	9.8	0.66	6.7
I	19.2	16.3–23.0	19.2	1.70	8.9
L	14.0	11.6–17.1	14.0	1.39	10.0



**Fig. 9.** Diagram of CED indicator calculated for kWp of photovoltaic installation.

It is necessary to point out that the DSSC configuration with steel support has been modeled on the basis of the prototype recently developed by Dyesol in collaboration with Tata Steel. This device is in an advanced research state and the steel structure has the double function of supporting the DSSC module and the roofing [104]. Its remarkable contribution to the indicators showed in this section is somewhat misleading in terms of its positive impact, because in this case one of the two supporting structures of the DSSC module works as a roofing element. For all the other modules, the impact related to roof building is not included in the assessment. Thus if the materials and energy required for roof building are considered in the analysis this would surely lead to a significant increase in impacts on the eco-profiles of all the other technologies.

In Fig. 10, the GWP100 indicator expressed as a function of the electric productivity (kWp) of the photovoltaic system is reported. In this case all DSSC devices perform comparably or even better compared to traditional inorganic thin film modules. Keeping in mind that the BOS contribution is likely to be overestimated for a roof-integrated installation at this level, it can be argued that DSSC environmental performances could be competitive with other thin film technologies even for module efficiency values between 6% and 8%.

Indeed one of the major limiting factors for DSSC technology industrial development and market establishment has been represented so far by the photoconversion efficiency decrease due to the support structure area increase. As demonstrated by Hinsch et al. [80] the manufacture of a  $60 \times 100 \text{ cm}^2$  module recently led to an efficiency of 2.3% which is a much lower value than that of a  $0.25 \text{ cm}^2$  single cell with the same structure. The pivotal issue for future DSSC development is bound to two factors that are strictly interconnected: the improvement of the efficiency on one hand and the drastic decrease of efficiency loss in the up-scaling process on the other. The low percentage of active area for a  $6000 \text{ cm}^2$  module is mainly responsible for such an efficiency drop. A 48% value of active area is clearly less competitive in comparison with inorganic thin film technologies that are generally characterized by a 100% value of active area. In their study, Hinsch and collaborators showed that significant improvements could be achieved by decreasing the total area of the module ( $100 \text{ cm}^2$ ) and, through simple structural tricks, modules with 7.1% efficiency could be obtained.

In this analysis, an up-scaling process capable of fabricating DSSC panels with at least a 75% active area has been supposed. This is the targeted value of active area which, together with technological improvements in terms of materials and fabrication techniques, could reasonably allow for the set-up and production of  $1 \text{ m}^2$  panels with 8% efficiency in relatively short times [141,142].

In Fig. 11, the EPBT for all technologies is reported. For an average yearly irradiation in Central Europe ( $1117 \text{ kWh/m}^2 \text{ year}$ ), values span from a minimum of 1.29 for the MCHP to a maximum of 3.33 years for the a-Si system, if we exclude the DSSC configuration with steel support that shows an EPBT of 3.88 years. As mentioned before, the latter is the only photovoltaic technology in the analysis that includes the architectural element on which the solar cell is supported. Thus the high EPBT value must not be considered as a negative result but as a global measure of a photovoltaic roof performance.

As can be seen from the diagram, in general EPBT values in terms of produced energy for the DSSC PET and DSSC glass system

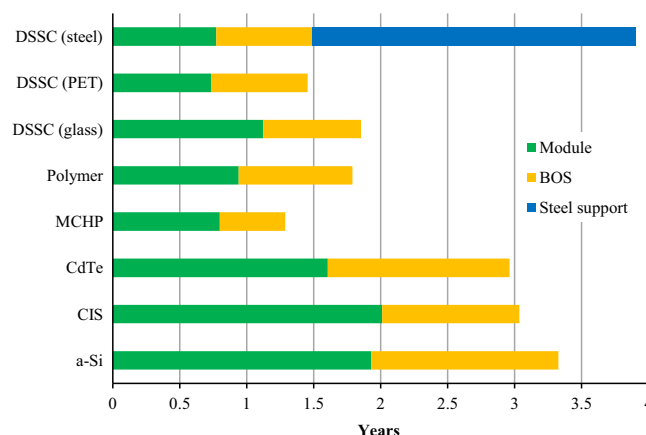


Fig. 11. Diagram of EPBT indicator calculated for the irradiation value of  $1117 \text{ kWh/m}^2 \text{ year}$  (Central Europe). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

compare very well with the best value obtained for the MCHP system along the series. If the attention is focused on the EPBT contribution of the module (green section of the histograms), we found a 0.73 value for the DSSC PET thus making this module the best performer, followed by the MCPH module with a 0.80 value. The 1.12 years computed for the DSSC glass still represents a good result that, differently from other mature and well-established technologies, is liable to improve by a wide margin thanks to the potential progress in both efficiency and technological aspects that DSSC could most likely experience in the near future. Concerning the EPBT contribution of BOS (yellow section of the histograms), the 0.72 years computed for the DSSC PET and glass systems can be considered as a threshold for such devices: the inclusion in the analysis of the suitable building integration solutions for the supporting of such systems would substantially reduce the weight of the BOS contribution for DSSCs. This might positively affect the photovoltaic performances of DSSC systems as well as for efficiency values like the one considered in this study.

To overcome the limit and uncertainty of results related to the geographic localization of the photovoltaic systems, a sensitivity analysis for different latitudes of the above mentioned indicators was performed. Calculations are based on the three average yearly irradiation levels typical for Europe as discussed in Section 4.3. In Figs. 12–14 the CED, GWP100 and EPBT indicators are reported, respectively.

## 6. End of life and recycling options

With the recent enormous development and diffusion of photovoltaic systems in the world, the collection and recycling of end-of-life modules have become fundamental issues for their environmental sustainability. In July 2012 the European Commission decided to include photovoltaics in the waste electrical and electronic equipment (WEEE) Directive establishing rules for collection, disposal and recycle of PV modules [143]. However, already in 2007 some of the world's largest photovoltaic industry had founded the PV Cycle Program to initiate an organize a European network for modules collection and recycling. By 2012, this organization covered nearly the 95% of the European solar market recycling activity, with 272 registered collection points and more than 5200 t of modules recycled [144]. Another example of recycling program is represented by the First Solar Programme [145].

The matter of recycling of panels will become pivotal in the next year due to the wide spread of photovoltaic systems in the world in the past 10 years. Considering the average 25–30 years

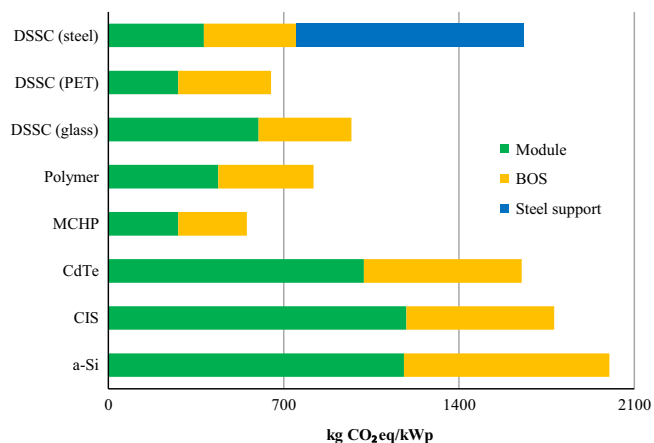
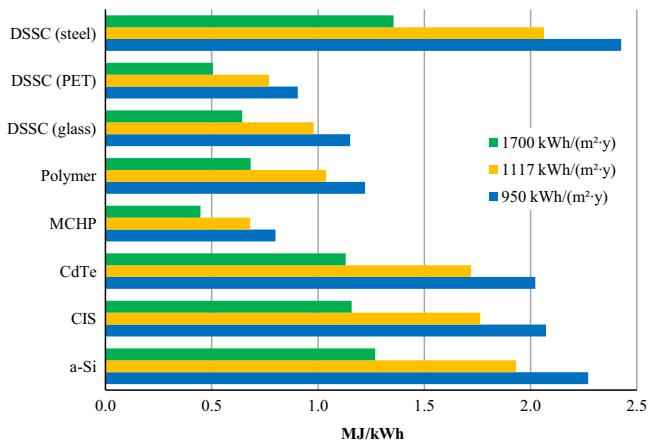
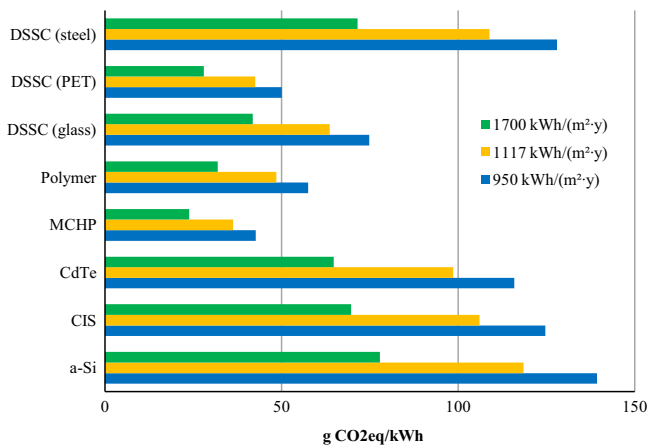


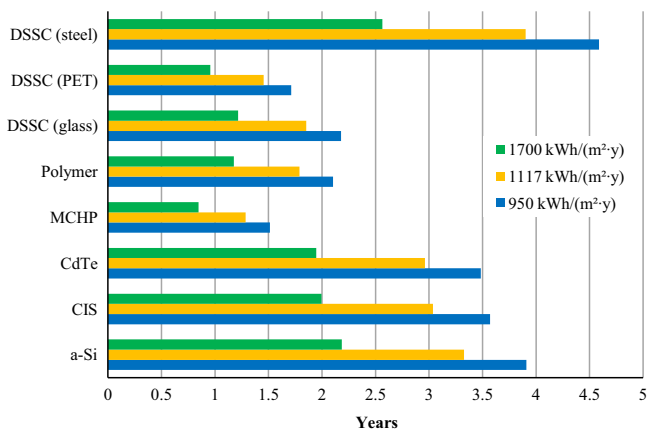
Fig. 10. Diagram of GWP100 indicator for kWp of photovoltaic installation.



**Fig. 12.** Diagram of CED indicator calculated for kWh electricity production of photovoltaic installation at different irradiation values.



**Fig. 13.** Diagram of GWP indicator calculated for kWh electricity production of photovoltaic installation at different irradiation values.



**Fig. 14.** Diagram of EPBT indicator calculated for different irradiation values.

life time of photovoltaic devices, there will be an exponential growth of module wastes between 2025 and 2030 [146].

In recent years many different studies reported the feasibility of different recycling processes [146–149]. For the total mass of photovoltaic installations, excluding BOS, the main contribution is given by the support material that represents over 80% of the panel depending on the technology. Glass recycling is a well-

established process that can be employed for all the photovoltaic technologies. Also recycling of the various polymers is accomplished through consolidated processes, but in this case, it would be somewhat more complicated to separate them from other materials present in a DSSC module. If the separation process is efficient, it is possible to recycle the polymer substrate in order to restrict the environmental impact of the modules.

On the other hand, the recycling techniques for the other components of a photovoltaic panel are much differentiated and, in some cases, still at the R&D stage. They require more time and efforts depending on the type and nature of the component. Regarding the semiconductor, each photovoltaic technology is based on a typical material (silicon in various crystalline forms, cadmium and tellurium, gallium and indium, titanium, etc.) that requires a particular separation and recycling processes. For DSSCs the semiconductor is generally formed by a nanostructured metal oxide, the most used being  $\text{TiO}_2$ . At present there are a lot of uncertainties regarding the chemical, physical and biological behavior of nanomaterials and nanotechnologies [150]. Moreover, the wide availability of  $\text{TiO}_2$  together with the predictable complexity of any recycling processes for stained semiconductors make this procedure theoretically unfavorable.

Another recyclable key component is the sensitizer [151], particularly for those configurations that includes metal-based dyes. Clearly, the recycling of metal represents the most important process from both an environmental and economic point of view.

Similar considerations can be made for the counter electrode component, generally based on platinum, because of the large expense associated with the extraction and manufacture of the metal.

Thus an efficient recycling process would be recommended and, for the same reasons, the substitution of platinum with another material could be beneficial [111,112,152].

Concerning the economic feasibility of the recycling process, it has been argued that for photovoltaics this process is economically unfavorable compared with landfill scenarios [146]. Anyway the environmental aspects cannot be underrated and photovoltaic technology will be essentially sustainable if all its components would be recyclable.

## 7. Conclusion

Among the innovative solar cells classified as emerging photovoltaics, DSSC technology has catalyzed great interest as a viable alternative to traditional systems. Such cells can offer significant economic and environmental advantages over conventional photovoltaics because they can be manufactured in a relative inexpensive way, energy efficiently and through eco-friendly methods.

The impressive work performed to find the right set of cell components for power-conversion efficiency increase and suitable structural architectures for larger device fabrication has led to a large number of different solutions at lab and pilot scale. Main advances from this R&D activity have allowed the manufacturing of solar systems that are now on the verge of commercialization.

In this paper, a recap of progress obtained at different scales has been reviewed for DSSCs from a LCA perspective. In fact the development of new technologies requires an overall evaluation of the product environmental impacts and benefits. LCA is one of the most powerful methods that allow an in depth understanding of the potential of innovative technologies in terms of environmental sustainability and a comparison with other more mature and best-established technologies.

Results obtained for cells and module manufacture were pivotal to characterize the hot spots and to highlight the opportunities for technical improvements of the whole production processes. In general the major impact is ascribable to the module support

materials and this can be reduced of about a 35% of energy consumption changing from glass to polymeric substrate. Other module components give minor contributions that largely depend on the physico-chemical characteristics of the raw material.

The study for the use phase of the life cycle have been performed to evaluate the photovoltaic performances of a virtual grid-connected roof-top solar system with the aim of comparing DSSC eco-profile with several thin film technologies. Major outcomes show that CED, GWP100 and EPBT values for DSSCs compare similarly and are sometimes better than inorganic thin film devices, even for a far-from-optimum industrial fabrication procedure. In fact an energy saving in the range between 48% and 66% and a reduction of CO<sub>2</sub> emissions in the range between 49% and 76% are achievable employing the DSSC module for photovoltaic installation. This turns out in an EPBT saving ranging from a minimum of 8 to a maximum of 14 months with respect to other thin film panels. The evaluation of these positive performances strengthens the assumption that DSSCs are an economically and environmentally viable alternative for photovoltaic solutions.

The focus on these potential advantages for DSSC along with their capability to exploit diffuse light and versatility of applications allows forecasting the potential for DSSCs to achieve and dominate different niches of the PV market especially in the building-integrated photovoltaics sector where DSSC low-light performances could translate into a substantial commercial advantage.

Actually, how DSSC devices will compete with their counterparts based on traditional photovoltaic technologies will depend on many factors such as scarcity of rare elements, availability of raw materials, cost-effective processing techniques and, obviously, the overall market demand.

Given that all different technologies will realistically coexist in the future PV market, we believe that an objective prediction for DSSCs evolution must be based on complementarity more than on competitiveness issues: the end-use and not the use-as-usual standard should be the common denominator for new photovoltaic technologies comparison.

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## References

- [1] Skotheim T. Dye sensitized solar-cells. US patent: 4 190 950; 1980.
- [2] O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. *Nature* 1991;353:737–40.
- [3] Shockley W, Queisser HJ. Detailed balance limit of efficiency of p–n junction solar cells. *J Appl Phys* 1961;32:510–9.
- [4] Snaith HJ. Estimating the maximum attainable efficiency in dye-sensitized solar cells. *Adv Funct Mater* 2010;20:13–9.
- [5] NREL: National Center for Photovoltaics, Research Cell Efficiency Records. (<http://www.nrel.gov/ncpv/>); 2013 [accessed on June 2013].
- [6] Peter LM. The Grätzel cell: where next? *J Phys Chem Lett* 2011;2:1861–7.
- [7] Burschka J, Pellet N, Moon SJ, Humphry-Baker R, Gao P, Nazeeruddin MK, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* 2013;499:316–20.
- [8] Gonçalves LM, Bermudez VdZ, Ribeiro HA, Mendes AM. Dye-sensitized solar cells: a safe bet for the future. *Energy Environ Sci* 2008;1:655–67.
- [9] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. *Chem Rev* 2010;110:6595–663.
- [10] Hardin BE, Snaith HJ, McGehee MD. The renaissance of dye-sensitized solar cells. *Nat Photonics* 2012;6:162–9.
- [11] Jung HS, Lee J-K. Dye sensitized solar cells for economically viable photovoltaic systems. *J Phys Chem Lett* 2013;4:1682–93.
- [12] Wang L, Fang X, Zhang Z. Design methods for large scale dye-sensitized solar modules and the progress of stability research. *Renew Sustain Energy Rev* 2010;14:3178–84.
- [13] Gong J, Liang J, Sumathy K. Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel material. *Renew Sustain Energy Rev* 2012;16:5848–60.
- [14] Pettersson H, Nonomura K, Kloo L, Hagfeldt A. Trends in patent applications for dye-sensitized solar cells. *Energy Environ Sci* 2012;5:7376–80.
- [15] Dyesol. (<http://www.dyesol.com/>); 2013 [accessed on June 2013].
- [16] First Solar. (<http://www.firstsolar.com/>); 2013 [accessed on June 2013].
- [17] G24 Innovations. (<http://www.g24i.com/>); 2013 [accessed on June 2013].
- [18] Solaronix. (<http://www.solaronix.com/>); 2013 [accessed on June 2013].
- [19] Fujikura. (<http://www.fujikura.com/>); 2013 [accessed on June 2013].
- [20] NLAB Solar. (<http://www.nlabsolar.com/>); 2013 [accessed on June 2013].
- [21] Oxford Photovoltaics. (<http://www.oxfordpv.com/>); 2013 [accessed on June 2013].
- [22] Peccell. (<http://www.peccell.com/>); 2013 [accessed on June 2013].
- [23] Sony. (<http://www.sony.net/>); 2013 [accessed on June 2013].
- [24] 3G Solar. (<http://www.3gsolar.com/>); 2013 [accessed on June 2013].
- [25] Solarprint. (<http://www.solarprint.ie/>); 2013 [accessed on June 2013].
- [26] Sharp Solar. (<http://www.sharp-solar.com/en/>); 2013 [accessed on June 2013].
- [27] Fraunhofer ISE. (<http://www.ise.fraunhofer.de/en/>); 2013 [accessed on June 2013].
- [28] Wei TC, Lan JL, Wan CC, Hsu WC, Chang YH. Fabrication of grid type dye sensitized solar modules with 7% conversion efficiency by utilizing commercially available materials. *Prog Photovolt: Res Appl* 2012. <http://dx.doi.org/10.1002/ppp.2252>.
- [29] Dyesol. Current commercialization projects and collaborations. (<http://www.dyesol.com/partners/current-projects/>); 2013 [accessed on June 2013].
- [30] G24i. Product specifications. (<http://www.g24i.com/pages/product-specifications,84.html>); 2013 [accessed on June 2013].
- [31] NanoMarket L. Dye-sensitized Cell Markets – Nano-531; 2012.
- [32] IEA. Technology roadmap: solar photovoltaic energy; 2010.
- [33] EPIA. Global Market Outlook for photovoltaics 2013–2017; 2013.
- [34] Martinot E, Cabraal A, Mathur S. World Bank/GEF solar home systems projects: experience and lessons learned 1993–2000. *Renew Sustain Energy Rev* 2001;5:39–57.
- [35] Nieuwenhout FDJ, Dijk Av, Dijk VAPv, Hirsch D, Lasschuit PE, Roelck Gv, et al. Experiences with solar home systems in developing countries. *Prog Photovolt: Res Appl* 2001;9:455–74.
- [36] Hashmi G, Miettinen K, Peltola T, Halme J, Asghar I, Aitola K, et al. Review of materials and manufacturing options for large area flexible dye solar cells. *Renew Sustain Energy Rev* 2011;15:3717–32.
- [37] Kelly CA, Meyer GJ. Excited state processes at sensitized nanocrystalline thin film semiconductor interfaces. *Coord Chem Rev* 2001;211:295–315.
- [38] Mishra A, Fischer MKR, Bauerle P. Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules. *Angew Chem Int Ed* 2009;48:2474–99.
- [39] Narayan MR. Review: dye sensitized solar cells based on natural photosensitizers. *Renew Sustain Energy Rev* 2012;16:208–15.
- [40] Kim HS, Im SH, Park NG. Organolead halide perovskite: new horizons in solar cell research. *J Phys Chem C* 2014;118:5615–25.
- [41] Harikisun R, Silvestro HD. Long-term stability of dye solar cells. *Sol Energy* 2011;85:1179–88.
- [42] Dessi A, Consiglio GB, Calamante M, Reginato G, Mordini A, Peruzzini M, et al. Organic chromophores based on a fused bis-thiazole core and their application in dye-sensitized solar cells. *Eur J Org Chem* 2013;10:1916–28.
- [43] Consiglio GB, Pedna F, Fornaciari C, Biani FFD, Marotta G, Salvatori P, et al. Assessment of new gem-silanediods as suitable sensitizers for dye-sensitized solar cells. *J Organomet Chem* 2013;723:198–206.
- [44] Zani L, Reginato G, Mordini A, Calamante M, Peruzzini M, Taddei M, et al. An unusual thiazolo[5,4-d]thiazole sensitizer for dye-sensitized solar cells. *Tetrahedron Lett* 2013;54:3944–8.
- [45] Greijer H, Karlson L, Lindquist SE, Hagfeldt A. Environmental aspects of electricity generation from a nanocrystalline dye sensitized solar cell system. *Renew Energy* 2001;23:27–39.
- [46] Wild-Scholten MJD, Veltkamp A. Environmental life cycle analysis of dye sensitized solar devices. Status and outlook. (<http://www.ecn.nl/>) ECN solar energy; 2007.
- [47] Fthenakis V, Alsema E. Photovoltaics energy payback times, greenhouse gas emissions and external costs: 2004 – early 2005 status. *Prog Photovolt: Res Appl* 2006;14:275–80.
- [48] Alsema E, Nieuwlaar E. Energy viability of photovoltaic systems. *Energy Policy* 2000;28:999–1010.
- [49] Fthenakis V, Kim HC. Photovoltaics: life-cycle analyses. *Solar Energy* 2011;85:1609–28.
- [50] Bravi M, Parisi ML, Tiezzi E, Basosi R. Life cycle assessment of advanced technologies for photovoltaic panel production. *Int J Heat Technol* 2010;28:129–35.
- [51] Bravi M, Parisi ML, Tiezzi E, Basosi R. Life cycle assessment of a micromorph photovoltaic system. *Energy* 2011;36:4297–306.

- [52] Raugai M, Bargigli S, Ulgiati S. Life cycle assessment and energy pay-back time of advanced photovoltaic modules: CdTe and CIS compared to poly-Si. *Energy* 2007;32:1310–8.
- [53] Azzopardi B, Mutale J. Life cycle analysis for future photovoltaic systems using hybrid solar cells. *Renew Sustain Energy Rev* 2010;14:1130–4.
- [54] Kim HC, Fthenakis V, Choi J-K, Turney DE. Life cycle greenhouse gas emissions of thin-film photovoltaic electricity generation. *J Ind Ecol* 2012;16:S110–21.
- [55] Pacca S, Sivaraman D, Keoleian GA. Parameters affecting the life cycle performance of PV technologies and systems. *Energy Policy* 2007;35:3316–26.
- [56] Peng J, Lu L, Yang H. Review on life cycle assessment of energy payback and greenhouse gas emission of solar photovoltaic systems. *Renew Sustain Energy Rev* 2013;19:255–74.
- [57] Cucchiella F, D'Adamo I. Estimation of the energetic and environmental impacts of a roof-mounted building-integrated photovoltaic systems. *Renew Sustain Energy Rev* 2012;16:5245–59.
- [58] Parisi ML, Maranghi S, Sinicropi A, Basosi R. Development of dye sensitized solar cells: a life cycle perspective for the environmental and market potential assessment of a renewable energy technology. *Int J Heat Technol* 2013;31:143–8.
- [59] ISO (International Organization for Standardization) 14040 standard. Environmental management-life cycle assessment-principles and framework; 2006.
- [60] ISO (International Organization for Standardization) 14044 standard. Environmental management-life cycle assessment-requirements and guidelines; 2006.
- [61] Prè Consultants, SimaPro 7.3.3. (<http://www.pre-sustainability.com/sima-pro-ica-software>); 2013 [accessed on June 2013].
- [62] Ecoinvent Centre, Database ecoinvent data v2.2, Swiss Centre for Life Cycle Inventories. (<http://www.ecoinvent.org/database>); 2013 [accessed on June 2013].
- [63] Goedkoop M, Heijungs R, Huijbregts M, Schryver AD, Struijs J, Zelm RV. ReCiPe 2008: main report revised. (<http://www.pre-sustainability.com>). Prè Consultants; 2012.
- [64] Althaus HJ, Bauer C, Doka G, Dones R, Frischknecht R, Hellweg S, et al. Ecoinvent reports no. 3. Implementation of life cycle impact assessment methods; 2010.
- [65] IPCC. Climate change 2007: the physical science basis. contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change; 2007.
- [66] Laleman R, Albrecht J, Dewulf J. Life Cycle Analysis to estimate the environmental impact of residential photovoltaic systems in regions with a low solar irradiation. *Renew Sustain Energy Rev* 2011;15:267–81.
- [67] Jungbluth N, Stucki M, Frischknecht R. Ecoinvent reports No. 6. Part XII photovoltaics v2.1. 2009.
- [68] Jungbluth N, Stucki M, Frischknecht R, Busser S. Ecoinvent reports No. 6. Part XII photovoltaics v2.2+. 2010.
- [69] Alsema E. Energy payback time and CO<sub>2</sub> emissions of PV systems. Practical handbook of photovoltaics. 2nd ed.. Oxford, UK: Elsevier Ltd; 2012; 1097–1117.
- [70] Fthenakis V, Frischknecht R, Raugai M, Kim HC, Alsema E, Held M, et al. International Energy Agency – methodology guidelines on life cycle assessment of photovoltaic electricity; 2011.
- [71] Liska P, Vlachopoulos N, Nazeeruddin MK, Comte P, Grätzel M. cis-Diaquabis (2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium (II) sensitizes wide band gap oxide semiconductors very efficiently over a broad spectral range in the visible. *J Am Chem Soc* 1988;110:3685–6–87.
- [72] Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Muller E, Liska P, et al. Conversion of light to electricity by cis-X2Bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X=Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline TiO<sub>2</sub> electrodes. *J Am Chem Soc* 1993;115:6382–90.
- [73] Nazeeruddin MK, Zakeeruddin SM, Humphry-Baker R, Jirousek M, Liska P, Vlachopoulos N, et al. Acid-base equilibria of (2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) complexes and the effect of protonation on charge-transfer sensitization of nanocrystalline titania. *Inorg Chem* 1999;38:6298–305.
- [74] Ito S, Murakami TN, Comte P, Liska P, Grätzel C, Nazeeruddin MK, et al. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. *Thin Solid Films* 2007;516:4613–9.
- [75] Hagberg DP, Marinado T, Karlsson KM, Nonomura K, Qin P, Boschloo G, et al. Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells. *J Org Chem* 2007;72:9550–6.
- [76] Hagberg DP, Edvinsson T, Marinado T, Boschloo G, Hagfeldt A, Sun L. A novel organic chromophore for dye-sensitized nanostructured solar cells. *Chem Commun* 2006;2245–7.
- [77] Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, et al. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science* 2011;334:629–33.
- [78] Caduff M, Huijbregts MAJ, Althaus HJ, Hendrix AJ. Power-law relationships for estimating mass, fuel consumption and costs of energy conversion equipments. *Environ Sci Technol* 2011;45:751–4.
- [79] Frischknecht R, Busser S, Krewitt W. Environmental assessment of future technologies: how to trim LCA to fit this goal? *Int J Life Cycle Assess* 2009;14:584–8.
- [80] Hinsch H, Veurman W, Brandt H, Aguirre RL, Bialecka K, Jensen KF. World-wide first fully up-scaled fabrication of 60 cm × 100 cm dye solar module prototypes. In: Proceedings of 26th European PV solar energy conference and exhibition. Hamburg, Germany: Fraunhofer ISE; 2011.
- [81] Kroon JM, Sommeling PM, Mansom HV, Hinsch A, Veurman W, Pettersson H, et al. Efficient and robust dye sensitized solar cells and modules – project final report. (<http://www.robustdsc.eu>); ECN Solar Energy; 2011.
- [82] Garcia-Valverde R, Cherni JA, Urbina A. Life cycle analysis of organic photovoltaic technologies. *Prog Photovolt: Res Appl* 2010;18:535–58.
- [83] Spath M, Sommeling PM, Roosmalen JAMV, Smit HJP, van der Burg NPG, Mahieu DR, et al. Reproducible manufacturing of dye-sensitized solar cells on a semi-automated baseline. *Prog Photovolt: Res Appl* 2003;11:207–20.
- [84] Sastrawan R, Beier J, Belledin U, Hemming S, Hinsch A, Kern R, et al. A glass frit-sealed dye solar cell module with integrated series connections. *Sol Energy Mater Sol Cells* 2006;90:1680–91.
- [85] Kang MG, Park NG, Park YJ, Ryu KS, Chang SH. Manufacturing method for transparent electric windows using dye-sensitized TiO<sub>2</sub> solar cells. *Sol Energy Mater Sol Cells* 2003;75:475–9.
- [86] Kumara GRA, Kaneko S, Konno A, Okuya M, Murakami K, Onwona-agyeman B, et al. Large area dye-sensitized solar cells: material aspects of fabrication. *Prog Photovolt: Res Appl* 2006;14:643–51.
- [87] Goldstein J, Yakupov I, Breen B. Development of large area photovoltaic dye cells at 3G solar. *Sol Energy Mater Sol Cells* 2010;94:638–41.
- [88] Solaronix. Dye solar cell technology. (<http://www.solaronix.com/technology/dyesolarcells/>); 2013 [accessed on June 2013].
- [89] G24i. Dye sensitized solar cell manufacturing. (<http://www.g24i.com/pages/manufacturing.77.html>); 2013 [accessed on June 2013].
- [90] Dyesol. Product catalogue. (<https://secure.dyesol.com/index.php?template=category-page&catid=22>); 2013 [accessed on June 2013].
- [91] Senthilkumar V, Vickraman P, Ravikumar R. Synthesis of fluorine doped tin oxide nanoparticles by sol-gel technique and their characterization. *J Sol-Gel Sci Technol* 2010;53:316–21.
- [92] Kellenberger D, Althaus HJ, Jungbluth N, Künniger T. Ecoinvent reports No. 7. Part XI flat glass products and Processes. 2007.
- [93] Mahshid S, Ghamsari MS, Askari M, Afshar N, Lahuti S. Synthesis of TiO<sub>2</sub> nanoparticles by hydrolysis and peptization of titanium isopropoxide solution. *Semiconduct Phys Quant Electron Optoelectron* 2006;9: 65–68.
- [94] Ito S, Chen P, Comte P, Nazeeruddin MK, Liska P, Pechy P, et al. Fabrication of screen-printing pastes from TiO<sub>2</sub> powders for dye-sensitized solar cells. *Prog Photovolt: Res Appl* 2007;15:603–12.
- [95] Bonhote P, Dias AP, Papageorgiou N, Kalyanasundaram K, Grätzel M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg Chem* 1996;35:1168–78.
- [96] Dupont J, Souza RFD, Suarez PAZ. Ionic liquid (molten salt) phase organometallic catalysis. *Chem Rev* 2002;102:3667–92.
- [97] Zakeeruddin SM, Grätzel M. Solvent-free ionic liquid electrolytes for mesoscopic dye-sensitized solar cells. *Adv Funct Mater* 2009;19:2187–202.
- [98] Marsh KN, Boxall JA, Lichtenhaler R. Room temperature ionic liquids and their mixtures – a review. *Fluid Phase Equilib* 2004;219:93–8.
- [99] Xi C, Cao Y, Cheng Y, Wang M, Jing X, Zakeeruddin SM, et al. Tetrahydrothiophenium-based ionic liquids for high efficiency dye-sensitized solar cells. *J Phys Chem C* 2008;112:11063–7.
- [100] Cao Y, Zhang J, Bai Y, Li R, Zakeeruddin SM, Grätzel M, et al. Dye-sensitized solar cells with solvent-free ionic liquid electrolytes. *J Phys Chem C* 2008;112:13775–81.
- [101] Komiya R, Han L, Yamanaka R, Islam A, Mitate T. Highly efficient quasi-solid state dye-sensitized solar cell with ion conducting polymer electrolyte. *J Photochem Photobiol A: Chem* 2004;164:123–7.
- [102] Park JH, Jun Y, Yun HG, Lee SY, Kang MG. Fabrication of an efficient dye-sensitized solar cell with stainless steel substrate. *J Electrochem Soc* 2008;155:F145–9.
- [103] Research and development on the dye-sensitized solar cell taking full advantage of the characteristics of the materials and aiming to open new markets. (<http://www.sony.net>); 2011.
- [104] Dyesol. 2012 Annual report. (<http://www.dyesol.com/investor-centre/company-reports>); 2013 [accessed on June 2013].
- [105] Sony. Research and development on the dye-sensitized solar cell taking full advantage of the characteristics of the materials and aiming to open new markets. ([http://www.sony.net/SonyInfo/technology/technology/theme/solar\\_01.html](http://www.sony.net/SonyInfo/technology/technology/theme/solar_01.html)); 2013 [accessed on June 2013].
- [106] Yang L, Wu L, Wu M, Xin G, Lin H, Ma T. High-efficiency flexible dye-sensitized solar cells fabricated by a novel friction-transfer technique. *Electrochem Commun* 2010;12:1000–3.
- [107] Sandoval-Paz MG, Ramirez-Bon R. Indium tin oxide films deposited on polyethylene naphthalate substrates by radio frequency magnetron sputtering. *Thin Solid Films* 2009;517:2596–601.
- [108] Heusing S, Oliveira PW, Kraker E, Haase A, Palfinger C, Veith M. Development of printed ITO coatings on PET and PEN foil for flexible organic photodiodes. *Org Optoelectron Photonics III* 2008;6999:699921.
- [109] Yamaguchi T, Tobe N, Matsumoto D, Nagai T, Arakawa H. Highly efficient plastic-substrate dye-sensitized solar cells with validated conversion efficiency of 7.6%. *Sol Energy Mater Sol Cells* 2010;94:812–6.
- [110] Hsu PY, Lee HF, Yang SM, Chua YT, Tung YL, Kai JJ. Highly efficient quasi-solid state flexible dye-sensitized solar cells using a compression method and light-confined effect for preparation of TiO<sub>2</sub> photoelectrodes. *Procedia Eng* 2012;36:439–45.

- [111] Wang M, Anghel AM, Marsan B, Ha NLC, Pootrakulchote N, Zakeeruddin SM, et al. CoS supersedes Pt as efficient electrocatalyst for triiodide reduction in dye-sensitized solar cells. *J Am Chem Soc* 2009;131:15976–7.
- [112] Chen J, Li K, Luo Y, Guo X, Li D, Deng M, et al. A flexible carbon counter electrode for dye-sensitized solar cells. *Carbon* 2009;47:2704–8.
- [113] Parakeva P, Kalderis D, Diamadopoulos E. Review – production of activated carbon from agricultural by-products. *J Chem Technol Biotechnol* 2008;83:581–92.
- [114] Noijuntura I, Kittisupakorn P. Life cycle assessment for the activated carbon production. In: Proceedings of the 2nd RMUTP international conference. Bangkok, Thailand; 2010.
- [115] Hagfeldt A, Cappel UB, Boschloo G, Sun L, Kloo L, Pettersson H, et al. Dye-sensitized photoelectrochemical cells. Practical handbook of photovoltaic. 2nd ed.. Oxford, UK: Elsevier Ltd; 2012; 479–542.
- [116] Balasingam SK, Lee M, Kang MG, Jun Y. Improvement of dye-sensitized solar cells toward the broader light harvesting of the solar spectrum. *Chem Commun* 2013;49:1471–87.
- [117] Xiang JH, Zhu PX, Masuda Y, Okuya M, Kaneko S, Koumoto K. Flexible solar-cell from zinc oxide nanocrystalline sheets self-assembled by an in-situ electrodeposition process. *J Nanosci Nanotechnol* 2006;6:1797–801.
- [118] Saito M, Fujihara S. Large photocurrent generation in dye-sensitized ZnO solar cells. *Energy Environ Sci* 2008;1:280–3.
- [119] Omar A, Abdullah H. Electron transport analysis in zinc oxide-based dye-sensitized solar cells: a review. *Renew Sustain Energy Rev* 2014;31:149–57.
- [120] Ou JZ, Rani RA, Ham MH, Field MR, Zhang Y, Zheng H, et al. Elevated temperature anodized Nb<sub>2</sub>O<sub>5</sub>: a photoanode material with exceptionally large photoconversion efficiencies. *ACS Nano* 2012;6:4045–53.
- [121] Li XD, Zhang DW, Chen S, Wang ZA, Sun Z, Yin XJ, et al. Enhancing efficiency of dye-sensitized solar cells by combining use of TiO<sub>2</sub> nanotubes and nanoparticles. *Mater Chem Phys* 2010;124:179–83.
- [122] Priya ARS, Subramania A, Jung YS, Kim KJ. High-performance quasi-solid-state dye-sensitized solar cell based on an electrospun PVdF-HFP membrane electrolyte. *Langmuir* 2008;24:9816–9.
- [123] Stathatos E, Lianos P, Zakeeruddin SM, Liska P, Grätzel M. A quasi-solid-state dye-sensitized solar cell based on a sol-gel nanocomposite electrolyte containing ionic liquid. *Chem Mater* 2003;15:1825–9.
- [124] Li B, Wang L, Kang B, Wang P, Qiu Y. Review of recent progress in solid-state dye-sensitized solar cells. *Sol Energy Mater Sol Cells* 2006;90:549–73.
- [125] Chung I, Lee B, He J, Chang RPH, Kanatzidis MG. All-solid-state dye-sensitized solar cells with high efficiency. *Nature* 2012;485:486–90.
- [126] Wang P, Zakeeruddin SM, Comte P, Exnar I, Grätzel M. Gelation of ionic liquid-based electrolytes with silica nanoparticles for quasi-solid-state dye-sensitized solar cells. *J Am Chem Soc* 2003;125:1166–7.
- [127] Fan K, Peng T, Chen J, Zhang X, Li R. A simple preparation method for quasi-solid-state flexible dye-sensitized solar cells by using sea urchin-like anatase TiO<sub>2</sub> microspheres. *J Power Sources* 2013;222:38–44.
- [128] Shi D, Pootrakulchote N, Li R, Guo J, Wang Y, Zakeeruddin SM, et al. New efficiency records for stable dye-sensitized solar cells with low-volatility and ionic liquid electrolytes. *J Phys Chem C* 2008;112:17046–50.
- [129] Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han L. Dye-sensitized solar cells with conversion efficiency of 11.1%. *Jpn J Appl Phys* 2006;45:L638–40.
- [130] Morooka M, Ogura R, Orihashi M, Takenaka M. Development of dye-sensitized solar cells for practical applications. *Electrochemistry* 2009;77:960–5.
- [131] Grätzel M, Poortmanws J, Durrant J, O'Regan B, Sariciftci S, Kroon J, et al. A technology roadmap towards stable & low-cost organic based solar cells; 2009.
- [132] Mason JE, Fthenakis V, Hansen T, Kim HC. Energy payback and life-cycle CO<sub>2</sub> emissions of the BOS in an optimized 3.5 MW PV installation. *Prog Photovolt: Res Appl* 2006;14:179–90.
- [133] Wild-Scholten MJD, Alsema E, Horst EWT, Bachler M, Fthenakis V. A cost and environmental impact comparison of grid-connected rooftop and ground-based PV systems. In: Proceedings of 21th European photovoltaic solar energy conference. Dresden, Germany; 2006.
- [134] Roes AL, Alsema EA, Blok K, Patel MK. Ex-ante environmental and economic evaluation of polymer photovoltaics. *Prog Photovolt: Res Appl* 2009;17:372–93.
- [135] Nawaz I, Tiwari GN. Embodied energy analysis of photovoltaic (PV) system based on macro- and micro-level. *Energy Policy* 2006;34:3144–52.
- [136] Moore LM, Post HN. Five years of operating experience at a large, utility-scale photovoltaic generating plant. *Prog Photovolt: Res Appl* 2008;16:149–259.
- [137] Cellura M, Longo S, Mistretta M. Sensitivity analysis to quantify uncertainty in Life Cycle Assessment: the case study of an Italian tile. *Renew Sustain Energy Rev* 2011;15:4697–705.
- [138] Yoon S, Tak S, Kim J, Jun Y, Kang K, Park J. Application of transparent dye-sensitized solar cells to building integrated photovoltaic systems. *Build Environ* 2011;46:1899–904.
- [139] Jelle BP, Breivik C, Røkenes HD. Building integrated photovoltaic products: a state-of-the-art review and future research opportunities. *Sol Energy Mater Sol Cells* 2012;100:69–96.
- [140] Chen RT, Chau JH, Hwang GL. Design and fabrication of diffusive solar cell window. *Renew Energy* 2012;40:24–8.
- [141] Green MA, Emery K, Hishikawa Y, Warta W, Dunlop ED. Solar cell efficiency tables (version 41). *Prog Photovolt: Res Appl* 2013;21:1–11.
- [142] Fukui A, Fuke N, Komiya R, Koide N, Yamanaka R, Katayama H, et al. Dye-sensitized photovoltaic module with conversion efficiency of 8.4%. *Applied Physics Express*. 2009;2:082202.
- [143] Directive 2012/19/EU of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE); 2012.
- [144] PV Cycle Annual Report 2012. (<http://www.pvcycle.org>); 2013 [accessed on June 2013].
- [145] First solar. The first global and comprehensive module recycling program. (<http://www.firstsolar.com/Sustainability/Environmental/Product-life-cycle-management/Recycling-Process>); 2013 [accessed on June 2013].
- [146] McDonald NC, Pearce JM. Producer responsibility and recycling solar photovoltaic modules. *Energy Policy* 2010;38:7041–7.
- [147] Müller A, Wambach K, Alsema E. Life Cycle Analysis of a solar module recycling process. In: Proceedings of 20th European photovoltaic solar energy conference. Barcelona, Spain; 2005.
- [148] Choi JK, Fthenakis V. Economic feasibility of recycling photovoltaic modules. *J Ind Ecol* 2010;14:947–64.
- [149] Fthenakis V. End-of-life management and recycling of PV modules. *Energy Policy* 2000;28:1051–8.
- [150] Som C, Berges M, Chaudhry Q, Dusinska M, Fernandes TF, Olsen SI, et al. The importance of life cycle concepts for the development of safe nanoproducts. *Toxicology* 2010;269:160–9.
- [151] Bae HG, Cho JY, Yang HC. Method for recycling dye of dye-sensitized solar cell module. WO2013/069929; 2013.
- [152] Kavan L, Yum JH, Grätzel M. Optically transparent cathode for dye-sensitized solar cells based on graphene nanoplatelets. *ACS Nano* 2011;5:165–72.